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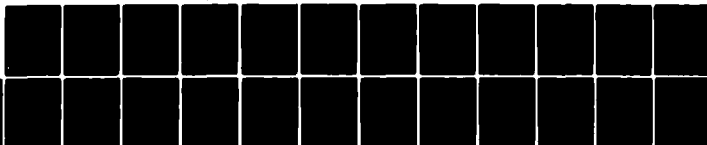
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THE ELECTROGENERATION OF SOLVATED METAL ATOMS. I. THE FAR INFRA--ETC(U)
AUG 81 P P SCHMIDT, B S PONS

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The far infrared spectrum of solvated lithium.

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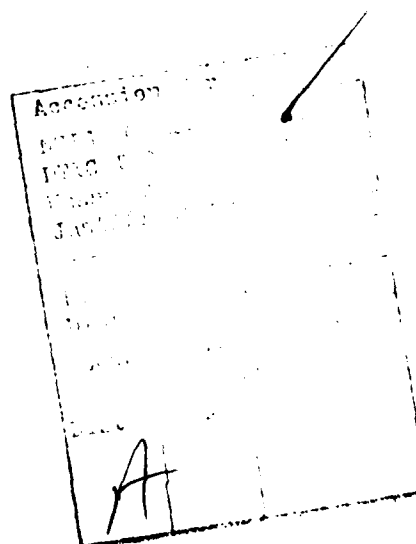
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The Electrogeneration of Solvated Metal Atoms. I.

The far infrared spectrum of solvated lithium

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Abstract

In some instances, the electrodeposition of metals onto electrodes may involve the prior generation of solvated metal atoms in the region of the outer Helmholtz plane. As a consequence, recently developed spectroscopic methods for detecting species in the interfacial region may be used to observe the solvated metal atoms. Therefore, with this paper we initiate an investigation of the nature of the possible states of solvation for these species in order to try to predict parameters which would be critical to their identification. In this paper we estimate the frequency at the band maximum for the far infrared-active vibrations which we predict to exist for the solvated lithium atom. We argue that the forces of repulsion may be nearly the same for the cation and atom. Thus, by means of a comparison to the Morse potential, we identify parameters for that potential. We determine the magnitude of the force constant for the vibrations of the atom in its cage of solvent. We suggest that the vibrational maximum for the solvated lithium atom may lie in the range of $300\text{-}400\text{ cm}^{-1}$. In addition, we have used an INDO calculation to examine the interaction between several solvent molecules and the lithium cation and atom. Although the INDO calculation is known not to yield accurate values for the vibrational force constants, we find nevertheless that a comparison of calculations for the cation and atom suggest that the solvated atomic frequency ought to lie only slightly below that of the solvated cation. This trend agrees with our prediction which is based on the use of a model potential energy function.

1. Introduction

The transfer of an electron in the process of the electro-reduction of a metallic cation ought to depend sensitively upon the location at which the reduction takes place. Moreover, the location of the reduction should have a strong influence upon the subsequent deposition of the metal atom. Thus, it is generally useful to know as much as possible about the site at which the electroreduction of a metallic cation takes place prior to its deposition onto the electrode surface. Armed with such knowledge, for example, it is possible to consider the manipulation of systems in order to obtain a variety of results.

If the reduction takes place at the outer Helmholtz plane in the electrical interface, then it should be possible to observe the spectral characteristics of the solvated metal atoms which are generated. The observed interfacial spectrum should reveal much about the nature of the environment of the atom. Over the past several years, spectral reflectance techniques have been developed to the stage where we believe it is possible to observe these atomic species.¹

At this time, we initiate an analysis of the states of solvation of the metallic cation and atom. In this paper we focus our attention on the lithium cation and atom. Our objective is to try to predict the magnitudes of quantities which are associated with these systems and which will be crucial in the experimental identification of the solvated atomic species. In the following sections we estimate the location and predict the shape of the absorption band in the far infrared which is associated with the

vibrations of the lithium atom within its cage of solvent. We suggest that the shape of the absorption band should differ substantially from that of the ion. It should be broad and reasonably featureless.

The rationale behind this analysis is the following. The major force which binds the solvent to the lithium cation is electrostatic. The attraction depends upon the direct ionic-dipolar interaction and upon the ionic-induced dipolar force. Short-ranged repulsions of a quantal origin also play a role. Indeed, we have shown^{2,3} that the far infrared spectra of the simple, solvated alkali metal cations can be explained adequately in terms only of the repulsion and the ionic-induced dipolar interaction. The repulsion can be expressed in terms of a Born-type of exponential form.²⁻⁴ For an ion which vibrates, trapped inside of a crystalline cage of solvent, there are no second order (harmonic) electrostatic contributions to the force field (in the sense of the Taylor series expansion of the complete potential). This result follows from the assumption of a regular crystalline arrangement for the distribution of solvent in the first shell. The reason for the vanishing of the electrostatic contributions to the vibrational analysis is due entirely to factors of symmetry.²

It is necessary to note the role of fluctuations in the locations of the solvent about their positions in the regular, crystalline structure of solvation. Deviations from the regular distribution yield net electrostatic contributions. Thus, obviously, in any actual system in which all species fluctuate about positions of optimal arrangement, electrostatic forces are important. However, if the symmetric distribution is indeed the most likely

distribution for the system, then the fluctuations on average contribute to broadening and the generation of an absorption band. In fact, an analysis of the vibrations of cations within distorted tetrahedral cages showed that the splitting of the vibrationally degenerate levels is not large.^{2b} The analysis of states of vibration for the solvated cation or atom carried out with reference to the optimal, symmetric configuration serve to identify the location of the band maximum.

The far infrared-active vibrations of the simple solvated cations are essentially independent of the solvent.⁵ The vibrations depend upon parameters which are associated with the short-ranged repulsions and the ionic-induced dipolar attractions, as indicated above. There is a functional correspondence between the form of the exponential repulsion and the repulsion in the Morse potential. Thus, if we are able to identify parameters which are associated with the exponential repulsion which operates for the solvated cation, and if we assume that this term alters minimally when the solvated metal atom is formed, then it is possible to identify values of the parameters which are associated with the Morse potential. In view of the fact that the direct ionic-dipolar interaction does not play a direct role in the determination of the magnitude of the force constant for the solvated cation, it seems reasonable to suspect that the solvated atom may depend upon a repulsive force of similar magnitude. This is the assumption we pursue in the following sections.

In the next section, we make the identification of the parameters in the Morse potential according to the suggestion just made.

It is possible, therefore, to determine the magnitude of the force constant which will be associated with the vibrations of the solvated atom. We find that indeed the atom should have a vibrational maximum near to the vibrational maximum which is associated with the solvated cation.

In the third section we present the results of several INDO calculations for the lithium cation and atom interacting with several solvents. Although INDO calculations do not yield numerically accurate, absolute values for vibrational force constants, we wanted to see if the computed force constants for the cation and atom interacting with a particular solvent followed a trend similar to that which we predicted with the use of the correspondence between the Born repulsion and the repulsive component in the Morse potential. As we show, the trend is effectively the same. The force constants predicted for the atom differ only slightly from those predicted for the cation on the basis of the INDO calculation.

2. Vibrations of the cation and atom in a cage of solvent

For species which strongly solvate the alkali metal cations, the locations of the experimental band maxima shift only slightly from one solvent to another.⁵ This observation supports the interpretation of the spectra as arising from the vibrations of the cations about their positions of equilibrium at the centre of the cage of solvent. The complete potential is constructed as the sum of pair-wise interactions which operate between the ion and the molecules of solvent. For a symmetric cage of solvent, it is easy to see that the location of the position of equilibrium coincides

with the centre of symmetry. From the centre of symmetry, vectors radiate uniformly to each of the molecules of solvent. Thus, the complete static potential energy of the ion at the centre of the distribution of primary solvent is

$$V(\underline{R}) = \sum_i v(\underline{R}_i) \quad (2.1)$$

where \underline{R}_i is the vector from the origin to the molecule i . The potential $v(\underline{R}_i)$ consists of parts which we assume contribute to the complete interaction: e.g., the Born exponential repulsion, ionic-dipolar interactions, etc.

In order to consider the vibrations of the centrally located, solvated cation, it is necessary to consider displacements about the end of each vector \underline{R}_i . Let the common displacement be \underline{r} . We consider

$$V(\underline{R}+\underline{r}) = \sum_i v(\underline{R}_i+\underline{r}) \quad (2.2)$$

and \underline{r} is common to each vector \underline{R}_i . The Taylor series can be constructed for each $v(\underline{R}_i)$. Thus, we write

$$v(\underline{R}_i+\underline{r}) = \sum_{n=0}^{\infty} \frac{1}{n!} (\underline{r} \cdot \nabla_{\underline{R}_i})^n v(\underline{R}_i). \quad (2.3)$$

This, in turn, is summed over the molecules of solvent.

We have shown elsewhere^{2,6-8} that the expansion (2.3) for a scalar function $v(\underline{R})$ is given by

$$v(\underline{R}+\underline{r}) = \sum_{n=0}^{\infty} (\underline{r}^n/n!) \sum_{\ell} A_{n\ell} P_{\ell}(\hat{\underline{r}} \cdot \hat{\underline{R}}) \sum_{q=0}^{\ell} \frac{(-1)^q (\ell+q)!!}{(\ell-q)!(2q)!!} R^{-q}$$

$$\times \left\{ \frac{n-q}{R} + \frac{d}{dR} \right\} \left(\frac{d}{dR} \right)^{n-q-1} v(R) \quad (2.4)$$

with

$$\begin{aligned} A_{n\ell} &= 0 \text{ for } \ell > n \text{ and } n-\ell \text{ odd} \\ &= \frac{(2\ell+1)n!(n-\ell+1)!!}{(n-\ell+1)!(n+\ell+1)!!} \text{ for } \ell \leq n \text{ and } n-\ell \text{ even.} \end{aligned} \quad (2.5)$$

$P_\ell(x)$ is the Legendre polynomial of order ℓ . The argument $\hat{r} \cdot \hat{R}$ of the Legendre polynomial is the scalar product of the unit vectors \hat{r} and \hat{R} . It is simply the cosine of the angle between these vectors.

Our interest focuses on the second order term, as it defines the harmonic potential, and, hence, the force constant. In general, for

$$v(\underline{R}_i) = \sum_j v_j(\underline{R}_i) \quad (2.6)$$

where j sums the components of the potential, viz., repulsive and attractive parts, we write

$$k_j(\underline{R}_{i0}) = \frac{1}{3} \left[\frac{2}{R} \frac{dv_j}{dR} + \frac{d^2 v_j}{dR_i^2} \right]_{R_{i0}} - \frac{2}{3} P_2(\hat{r} \cdot \hat{R}_i) \left[\frac{1}{R} \frac{dv_j}{dR_i} - \frac{d^2 v_j}{dR_i^2} \right]_{R_{i0}} \quad (2.7)$$

for the contribution to the force constant from the j^{th} part of the complete potential and the i^{th} source. The specification of \hat{r} defines the sense of the force constant.

For a regular tetrahedron of sources, for example, it is possible to show that for any well-behaved, scalar potential,

$$\sum_{(\text{tetrahedron})} p_2(\hat{r} \cdot \hat{R}_i) = 0. \quad (2.8)$$

Thus, the force constant reduces to

$$\begin{aligned} {}^*k_{(0)j} &= \sum_i k_j(R_{i0}) \\ &= \frac{4}{3} \left(\frac{2}{R} \frac{dv_j}{dR} + \frac{d^2v_j}{dR^2} \right)_{R_0} \end{aligned} \quad (2.9)$$

where R_0 now is the common length of each vector from the centre of symmetry to the source. A similar result is obtained for the regular octahedron, etc.

The exponential repulsion is

$$v_B(R) = B \exp[(R_0 - R)/\rho] \quad (2.10)$$

in which R_0 and ρ are characteristic of the interaction. In our work,^{2,3} we have taken R_0 to be the radius of solvation which is defined as the sum of the ionic (Goldschmidt) radius and the radius of the solvent as determined from the molar volume.^{9,10} The contribution of this term to the force constant for the regular tetrahedron is

$${}^*k_B = \frac{4}{3} \frac{B}{\rho^2} (1 - 2\rho/R_0). \quad (2.11)$$

The contribution of the ionic-dipolar direct interaction term vanishes, as mentioned.² The demonstration of this uses the

Carlson-Rushbrooke¹¹ expansion. The details are given elsewhere.²

The third major contribution to the potential comes from the ionic-induced dipolar interaction. This term has the form

$$v_{IID}(R) = - \frac{\alpha(Ze)^2}{2R^4} \quad (2.12)$$

where α is the polarizability of the solvent. The contribution this term in the potential makes to the force constant is

$$^4k_{IID} = - 8 \frac{\alpha(Ze)^2}{R_0^6} . \quad (2.13)$$

In considering the solvated atom, we make use of the Morse potential:

$$v_M(R) = D \exp[a(R_0-R)] \{ \exp[a(R_0-R)] - 2 \} . \quad (2.14)$$

Our choice of this potential is dictated by its mathematical simplicity, and primarily by a seemingly close correspondence between the Born repulsion $B \exp[(R_0-R)/\rho]$ and the repulsive component of the Morse potential: $D \exp[2a(R_0-R)]$. If we can substantiate the following identification

cation	→	atom
B	→	D
ρ	→	$1/2a$,

then we can estimate the order of magnitude of the force constant for the vibrations of the atom in its cage of solvent. From eqs (2.14) and (2.9), we find

$${}^4k_M = \frac{8a^2D}{3}. \quad (2.15)$$

The objective is to estimate 4k_M and with it, the frequency at the band maximum for the atom.

With only the value of the force constant for the far infrared-active vibration, it is possible to fit two parameters in a model potential energy function.³ In fact, we always have a second (virtual) datum, viz., the value of the net force at a point of equilibrium. The expression for the force together with the force constant allows us to find B and ρ , for example, in a potential function which depends in part on the Born exponential type of repulsion. This procedure was followed in a recent investigation of several possible forms for the potential energy function for the solvated alkali metal cations.³ One potential energy function consisted of the exponential repulsion, the ionic-dipolar direct interactions, the ionic-induced dipolar interactions, and a dipolar repulsion which operates between the dipoles of the solvent. For the lithium cation dissolved in dimethyl sulphoxide (DMSO), we found $B = 0.51 \times 10^{-12}$ erg and $\rho = 0.26 \text{ \AA}$. With the use of these values, we estimate 4k_M to be

$$\begin{aligned} k_M &\approx 2B/3\rho^2 \\ &= 50300 \text{ dyn cm}^{-1}. \end{aligned} \quad (2.16)$$

This value of the force constant corresponds to a frequency at the band maximum of 353 cm^{-1} .

In our initial consideration of the far infrared-active vibra-

tions of the alkali metal cations,² we simply related the Born and ionic-dipolar terms. As the determination of B and ρ amounts to parameter-fitting, this is an acceptable path to follow, if not altogether physically realistic. The consequence of this approach is the determination of values of B and ρ which are smaller in magnitude compared to the values quoted above. Specifically, we found $B = 0.23 \times 10^{-12}$ erg and $\rho = 0.19 \text{ \AA}$. These values suggest a frequency of 320 cm^{-1} at the band maximum for the solvated lithium atom.

The values we quote here for the frequency at the band maximum suggest only that the far infrared-active frequency should lie somewhere in the range of $300\text{-}400 \text{ cm}^{-1}$. It is certainly possible that even higher or lower limits are possible. However, we believe at this time that if the solvated atom exists, the frequency observed ought to be near the quoted range.

It is necessary to note a possible complication. The gas-phase vibration of Li_2 is known to be 352 cm^{-1} .¹² Although it is reasonable to expect that through the interaction with the solvent this value will be lower than that for the gas phase, it should not be much lower. Thus, simply to observe new spectral activity in the $300\text{-}400 \text{ cm}^{-1}$ range does not constitute proof of the existence of the solvated atom. Isotopic shift effects are ambiguous for this system as well. It may be necessary additionally to examine the spectra in the visible and ultraviolet regions in order conclusively to resolve the existence of solvated Li against the solvated molecule Li_2 .

Finally, with respect to this part of the analysis of the spectrum of the solvated lithium atom, we estimated the form of

of an intensity profile, or line-shape, for the system. We assumed that the solvated atom would be most sensitive to changes in the structure of the shell of solvent. The interaction of the atom with the remainder of the continuum solvent was ignored. Thus, we considered a cluster consisting of the atom surrounded by four fluctuating molecules of solvent.

For a given, randomly generated configuration of solvent, the atom was allowed adiabatically to seek its position of equilibrium within the cluster. This point was determined only for the atom. Randomly generated configurations of solvent generally lie far from states of equilibrium for the cluster.

Once the atom was located at its point of equilibrium, spherical oscillator basis functions were used in a variational estimate of the vibrational ground and first excited states. The oscillator strength was computed for the transition. The term was then weighted with a Boltzmann factor which was normalized to the (assumed optimal) tetrahedral configuration. Altogether, the result of the calculation indicated the appearance of a broad band which extends to considerable distances either side of the vibrational maximum. The effect of the inclusion of an interaction with the remainder of the (continuum) solvent is expected to make little further change of this line-shape.

In contrast, the spectrum of the ion is known to be asymmetric and reasonably sharply defined.⁵ This sharpness of definition of the line-shape may be a manifestation of the strength of interaction of the ion with the continuum modes of the polar medium such as is known to occur with the solvated electron.^{13,14}

3. INDO calculations

The lithium cation has been studied in a variety of aprotic solvents. Among the solvents which are important for electrochemical applications are acetonitrile, dimethylformamide, dimethylsulphoxide, and tetrahydrofuran, to name only a few. We have carried out INDO (incomplete neglect of differential overlap¹⁵) calculations on three systems: acetonitrile/lithium, diethyl ether/lithium, and THF/lithium. In our calculations, we determined the equilibrium separation between the lithium species (cation or atom) and the solvent, but did not optimize the geometry of the solvent in the presence of either the cation or atom of lithium. Instead, we made use of the standard bondlengths and angles¹⁵ to get a reasonable approximation of the energy of the solvent. We assumed that the important interaction is that between lithium and nitrogen in acetonitrile, and between lithium and oxygen in THF and diethyl ether. In each of these cases, the lithium was displaced along the axis of two-fold symmetry for the system of the lithium and solvent.

Schuster et al.¹⁶ have compared the CNDO/INDO and ab initio (Gaussian 70) calculations for the interaction between the lithium cation and several aprotic solvents. The CNDO/INDO calculations predict some participation of the electrons on the lithium cation in the association with the solvent. We found that our INDO calculations behaved similarly. In contrast, the ab initio calculations indicate essentially no delocalization of electronic charge on the lithium cation; the cation has effectively a zero polarizability and acts as a classical charged sphere. Moreover, it is known

that the predicted force constants for molecular vibrations found with the use of the CNDO/INDO schemes are generally too large.¹⁵ In spite of these deficiencies in the INDO scheme, we wanted to see if the same trends in the interaction between the lithium species and the solvent would be predicted.

In order to preserve a level of simplicity in the calculations, we considered only the interaction between a single molecule of solvent and the lithium cation or atom. We estimated the force constant for the displacement of these lithium species along the two-fold axis of symmetry defined by the solvent and lithium. Such an approach, we believe, ought to be diagnostic and ought to reveal any obvious trends.

We manipulated the data in several ways. First, we simply fitted the calculated potential (calculated with the INDO scheme) to a quadratic function in the region of the minimum in the energy. This minimum itself was found with the use of a quadratic interpolation. The force constant then was estimated for points which were displaced $0.05\overset{\circ}{\text{Å}}$ on either side of the minimum. The results of these calculations are displayed in Table 1. We find that the force constants and frequencies for the displacement of the cation and atom appear to follow the same trend as suggested by the examination of the model potential energy functions in the last section. In each case, the frequency for the solvent-lithium atom stretch is lower than the frequency for the solvent-lithium cation stretch by only a relatively small degree (tens--as opposed to hundreds--of wavenumbers). Thus, apparently there are associations of similar strength which operate in both the case of the solvated cation and atom.

For the case of the interaction of a lithium atom and a molecule of solvent, it is possible to fit the calculated potential (found by means of the INDO scheme) to the Morse potential. If in the Morse potential, eq (2.14), we write

$$a(R_0 - R) = x, \quad (3.1)$$

and let

$$y = \exp(x), \quad (3.2)$$

then

$$\begin{aligned} m(x) &= v_M(x)/D \\ &= y(x)[y(x) - 2]. \end{aligned} \quad (3.3)$$

It is clear that for a given value of x , $m(x)$ is a universal (dimensionless) function. Thus, if for an arbitrary potential the dissociation energy is known, then the function $m(x)$ can be determined according to (3.3). For any single value of $v(x)$, we construct an associated function $m(x)$ by dividing by the dissociation energy. If we assume that this function matches $m(x)$ defined by (3.3), we can find x from

$$x = \ln[1 \pm \sqrt{1+m(x)}]. \quad (3.4)$$

If, further, R_0 is known, then a can be found.

For the interaction of Li^0 with the solvents, we derived the

values given in Table 2. We found the value of $1/a$ for two values of R on either side of the minimum R_0 . This was done in the same sense as the quadratic fit discussed above. Although three points are needed for the quadratic fit, only two points are needed to fit the Morse potential (excluding the energy at infinite separation). Nevertheless, for acetonitrile, for example, we tested the fit by calculating $1/a$ for a large number of points which were generated by the INDO programme. We found the Morse potential fits the calculated potential well over quite a range of values of the displacement. The goodness of fit was determined simply by observing the constancy of the values of $1/a$ determined.

Once we determined the values of the parameters for the Morse potential, we were able to determine the value of the force constant for the lithium atom in a cage of solvent. The values of the frequency of the far infrared-active vibration at the band maximum were then estimated. These are close to the frequencies determined for the linear Li^0 -solvent complex.

For the case of the ion, on the other hand, it is not possible simply to fit the calculated potential energy function to the Morse potential. In order to carry out a final comparison of our empirical estimation--contained in the last section--with the estimates obtained with the use of the INDO scheme, we did the following. We used the INDO-predicted force constants for the cation-solvent linear stretch in the same type of analysis as used in reference 3 to determine the values of the parameters in the Born component in the model potential. Once B and ρ were found, a comparison to the Morse potential was made. We then estimated the frequency for the solvated atom.

The model potential has the form

$$V(R) = B \exp[(R_0 - R)/\rho] - \mu e/R^2 - \alpha e^2/2R^4 \quad (3.5)$$

where μ is the dipole moment, e is the electronic charge and α is the polarizability of the solvent. The condition for equilibrium yields the ratio B/ρ :

$$B/\rho = 2\mu e/R_0^3 + 2\alpha e^2/R_0^5. \quad (3.6)$$

The force constant is

$$k = B/\rho^2 - 6\mu e/R_0^4 - 10\alpha e^2/R_0^6. \quad (3.7)$$

Eq (3.6) determines the ratio B/ρ which can be used in eq (3.7) to find $1/\rho$ as follows:

$$\begin{aligned} 1/\rho &= \{k + 6\mu e/R_0^4 + 10\alpha e^2/R_0^6\}(\rho/B) \\ &= \frac{1}{R} \left(\frac{kR_0^6 + 6\mu eR_0^2 + 10\alpha e^2}{2\mu eR_0^2 + 2\alpha e^2} \right). \end{aligned} \quad (3.8)$$

Once ρ is known, B can be found. Finally, making the same type of comparison to the Morse potential as made in the last section, we find

$$k_{(\text{predicted})} = B/2\rho^2 \quad (3.9)$$

for the atom.

The results of the application of these formulae to the INDO-generated data are listed in Table 3. In this case, we see that the predicted force constants for the atom are larger than those found for the cation (by INDO) for these species dissolved in the ethers (THF and diethyl ether). The differences, however, still are relatively small. On the other hand, for acetonitrile the atomic frequency is predicted to lie at a lower value than the cationic frequency.

4. Discussion and conclusions

That there should exist any kind of factor which is common to the association of the cation and the solvent, and to the atom and the solvent would seem to be an unusual occurrence. In spite of the substance the INDO calculations give to the similarity in the force constant for the lithium cation and atom, this similarity needs to be examined further.

To begin, we note the fact that the binding energy for the solvent to the cation and the binding energy for the solvent to the atom ought to differ by an large amount. There is no aspect of our argument concerning the similarity of the force constants which contravenes this expectation. It is of course well known that the low-order molecular vibrations are accurately accounted for with the use of harmonic oscillator potential energy functions. The force constant in this function, as determined with the use of the Taylor series expansion of any arbitrary real potential energy function, is a measure of the radius of curvature of that function in the region of the minimum in the potential. Although it is possible

that the actual expression for the force constant may depend upon the dissociation energy, as is the case for the Morse potential, it is by no means certain that this is a general physical or mathematical requirement. Thus, it is entirely possible for two potential energy functions, with widely differing values for the dissociation energy, to have similar values for the calculated harmonic oscillator force constant. If the overall distribution of mass remains the same, as would be the case for a simple change in oxidation state, the species can exhibit similar values for the frequency at the maximum in the far infrared absorption band.

On the other hand, the line-shape for the absorption should differ for an atom as opposed to the ion by a considerable amount. The line-shape is governed more by the overall strength of the interaction between species and less by the curvature of the potential energy function at the energy minimum. In particular, in a system in which there are weak interactions, the system as a whole will be more susceptible to collisionally induced molecular distortions. Thus, if the overall binding of a molecule of solvent to an atom in solution is weaker than the binding of the cation to the same solvent, we expect to see a greater number of strongly distorted configurations for the atomic system.

Whether the similarity in magnitude of the atomic and cationic force constants is general or not needs to be explored. We can rationalize the similarity by arguing that the short-ranged repulsion is largely a function of the positive nuclear core of the lithium and the complete shell of 1s electrons. If the additional 2s electron in atomic lithium is sufficiently diffuse, then one would not expect this additional electron to have a

profound effect on the short-ranged interactions. At this time, we are not able to provide any more insight into the origin of the similarity in the force constants than we have already done.

The idea that the solvated atomic species can be formed is not as alien as one might expect at first. Zero-valent complexes have been known to exist for some time.¹⁷ Thus, for example, it is well-known that the direct reduction of silver cation in aqueous solution yields microcrystalline deposits. On the other hand, the electroreduction of silver in the presence of cyanide ion results in the formation of specularly reflective silver surfaces. Such reductions, it would seem, result from the slow, controlled deposition of the silver metal atoms as they are formed. This, we surmise, can best take place if silver is reduced to a dissolved, zero-valent state of atomic silver.

Finally, it is worth indicating the reason behind the examination of the INDO calculations for the two ethers, tetrahydrofuran and diethyl ether. Koch et al.¹⁸ recently examined the use of mixtures of THF in diethyl ether (approximately 5% THF) in lithium batteries. The results of their investigations indicate that there is a significant improvement in the performance of the batteries with the use of these solvents. It is assumed that the THF preferentially solvates the lithium cation. Moreover, Koch et al. report¹⁸ that the lithium surfaces generated in these battery systems are specularly reflective.

It is interesting to us to note that the INDO calculations seem to indicate that the direct interaction between diethyl ether and the lithium cation is marginally stronger than the interaction between the cation and THF. Thus, diethyl ether ought to solvate

the cation preferentially. If, to the contrary, THF actually does solvate preferentially, then the reason would seem to be tied to the enforced compact structure of the ether THF as opposed to the diethyl ether. Both diethyl ether and THF are essentially the same in terms of atomic composition. THF, however, is constrained to be a cyclic molecule. In contrast, in diethyl ether numerous, space-filling configurations are possible. Therefore, it seems likely to be the case that the THF molecules can more effectively solvate the lithium cation, as it is possible to pack--on average--more THF molecules about the cation. Thus, if the free energy of solvation of lithium by THF is more negative than is the case for diethyl ether, we suspect that the difference ought to be manifested in a large entropy factor for THF as opposed to the diethyl ether.

In conclusion, we reaffirm our belief that there is every reason to expect that some metal cations will be reduced at the outer Helmholtz plane to form effectively free, solvated atoms. It should be possible to observe these species by spectroscopic methods. Therefore, we have provided arguments which suggest the region of the spectrum in which we would initially expect to see the band maximum for the solvated atomic species of lithium.

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Table 1: Force constants and frequencies from INDO calculations

	THF	DEE	ACN
Cation	229,637 dyn cm ⁻¹ (781 cm ⁻¹)	245,305 (806)	193,549 (741)
Atom	205,031 (738)	217,182 (759)	175,532 (706)

THF:tetrohydrofuran, DEE:diethyl ether, ACN:acetonitrile

Table 2: Parameters for the Morse potential as determined by fitting to the INDO-generated potential

	THF	DEE	ACN
R ₀	2.092 Å	2.124	2.113
D	6.93 x 10 ⁻¹² erg	8.039 x 10 ⁻¹²	5.93 x 10 ⁻¹²
1/a	0.82 Å	0.86	0.82
k	273,101 dyn cm ⁻¹	289,858	235,178
freq.	823 cm ⁻¹	848	764

Table 3: Predicted parameters for the Morse potential as determined from INDO-generated data for the ion

	THF	DEE	ACN
R ₀ ^a	2.065 Å	2.088	2.093
k _{ion} ^a	229,637 dyn cm ⁻¹	245,305	193,549
α ^b	8 Å	10.4	4.4
μ ^c	1.7 debye	1.15	3.37
B	2.76 x 10 ⁻¹² erg	3.21 x 10 ⁻¹²	2.02 x 10 ⁻¹²
ρ	0.24 Å	0.24	0.24
k _{atom}	247,391 dyn cm ⁻¹	276,221	182,359
freq	811 cm ⁻¹	849	701

a. found with the use of the INDO calculation

b. found from the refractive index and the use of the
Lorentz-Lorentz equation:

$$\frac{n^2 - 1}{n^2 + 2} V_m = 4\pi\alpha/3 \quad V_m = \text{molar volume}$$

c. values from the Handbook of Physics and Chemistry
(Chemical Rubber Publishing Co.

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